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On the question of developing a common method of calculating salinity of sea water by specific electroconductivity, temperature and hydrostatic pressure

V. I. Zaburdaev and P. A. Kalashnikoff

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ABSTRACT

In this article a serial scheme is proposed for salinity calculation $X_{s,t,p} \rightarrow R_{s,t,0} \rightarrow R_{s,15,0} \rightarrow S$ and estimation is made of its maximum error. The influence of differing units of temperature measurement and electroconductivity on the calculation error of salinity is considered.

Introduction

The introduction of automated oceanographic systems measuring *in situ* the specific electroconductivity, temperature and hydrostatic pressure, requires an exact knowledge of the relationship between the parameters being measured and the salinity of seawater. At the present time there is no generally accepted method of calculating salinity from the results of *in situ* measurements, or on the use of the various empirical relationships [1, 4, 5, 10-13, 18, 20, 21], which are based on the results of fundamental research [6-8, 19, 22].

In reference [23] nine methods are compared for calculating salinity and it is shown that they all satisfactorily agree in the region of salinity 30-40 $^{\circ}/_{\circ\circ}$ and temperature +15°C. When there is a significant deviation from these values the divergences begin to exceed the errors quoted by the authors. Walker notes the following reasons for these divergences:

1. The disagreement between the values chosen for the specific electroconductivity of seawater of salinity 35 $^{\circ}/_{\circ\circ}$ at temperature 15°C and atmospheric pressure.
2. The application of various international temperature scales (IPTS 1948 and IPTS 1968) for expressions giving the temperature dependence of specific electroconductivity of normal water.
3. The difference of polynoms giving salinity as a function of specific electroconductivity at temperature 15°C.
4. The limited ranges of temperature, salinity, and pressure outside which the formulas give an incorrect calculated salinity.

To these causes it is essential to add four more possible sources of disagreement.

5. The differences in specific electroconductivity when measured in units of international or absolute ohms.
6. Differences in analytic expressions giving the temperature dependence of normal water, obtained on the basis of research from references [7, 19, 22].
7. The divergence between corrections, Δ_{15}, for converting the relative electroconductivity at any temperature to the specific

electroconductivity at 15°C, obtained from the research in references [7, 8].

8. The decrease in accuracy of the analytic expression giving the dependence of specific electroconductivity on pressure as a result of simplifying the expression recommended in reference [6].

All the enumerated sources of deviation of the different methods of calculating salinity are explained either by the subjective mode of treatment of the authors on the choosing of basic parameters and analytical expression, or the peculiarities of the fundamental research: a) the limits of measurements which define the ranges of salinity, temperature and electroconductivity and pressure, such that they do not account for the range of the indicated parameters and real conditions of the world ocean; b) difference in technology and accuracy of measurement (see Table).

To develop one (generally accepted) method of calculating salinity without ambiguity and guaranteeing the unanimity of measurement, the authors of this paper suggest a scheme of calculating salinity from in situ measurement of specific electroconductivity, temperature and pressure, based on the results of objective analysis of the existing relevant fundamental research.

Scheme for Calculating Salinity

In developing one scheme of calculating salinity it is desirable to proceed on the basis of the following objectives: physical clarity of equations used for transformation; the continuity of established concepts and expressions already accepted in the practice of oceanological work in the way of "standards"; the simplicity and convenience of the correction of the scheme in the event of the appearance of a new and more accurate data base on the relationship between electroconductivity, salinity, temperature, and pressure.

On the basis of the analysis of published material, two schemes of calculation have appeared:

$$X_{s,t,p} \rightarrow R_{s,t,0} \rightarrow R_{s,15,0} \rightarrow S \qquad (1)$$

$$X_{s,t,p} \rightarrow R_{s,t,0} \rightarrow R_{s,0,0} \rightarrow S \qquad (2)$$

where $X_{s,t,p}$ - the measured in situ specific electroconductivity of water with salinity S, at temperature t, and pressure P; $R_{s,t,0} = X_{s,t,0}/X_{35,t,0}$ is the ratio of the relative electroconductivity of water with salinity S, at temperature t, and atmospheric pressure (P=0) with the electroconductivity

$X_{35,t,0}$ of normal water of salinity 35 °/₀₀ at the same values of temperature and pressure; $R_{s,15,0} = R_{s,t,0} + \Delta_{15}$ is the relative electroconductivity of water brought to temperature 15°C; $R_{s,0,0} = R_{s,t,0} = \Delta_0$ is the relative electroconductivity of water, brought to temperature 0°C. The differences are contained in the calculation formulas of the consecutive operations indicated (either the articulated calculation (1) and (2), or one analytical expression replacing this step-by-step method [20,21]) and in the method of calculating the first step $X_{s,t,p} \to R_{s,t,0}$.

The conversion of specific electroconductivity $X_{s,t,p}$ to relative electroconductivity $R_{s,t,0}$ may be accomplished by the following methods:

$$X_{s,t,p} \to [X_{s,t,p}/f(P,t,X_{s,t,p}) = X_{s,t,0}] \to [X_{s,t,0}/X_{35,t,0} = R_{s,t,0}] \quad (3)$$

$$X_{s,t,p} \to [X_{s,t,p}/X_{35,t,p} = R_{s,t,p}] \to [R_{s,t,p} + \Delta_p = R_{s,t,0}] \quad (4)$$

where $f(P,t,X_{s,t,0})$ is the dependence of specific electroconductivity on pressure; $R_{s,t,p}$ is the relative electroconductivity in situ; Δ_p is the correction for pressure in converting the relative electroconductivity $R_{s,t,p}$ to atmospheric pressure.

The sequence (2) and (3) is presented in reference [18] for Northern Canadian waters with temperature -2°C to 20°C and sequence (4) (expressions for relative electroconductivity $R_{s,t,p}$ and correction Δ_p) is examined in reference [1]. We will note that the introduction of the expression for the relative electroconductivity $R_{s,t,p}$ is based on the extension of the well-known relationship for the relative electroconductivity $R_{s,t,0}$ at atmospheric pressure into the region of hydrostatic pressure, in this way correction Δ_p is analagous to correction Δ_{15}. In references [4, 13], the sequences of calculation presented are somewhat different from (3) and (4) and $R_{s,t,0}$ occupies an intermediate position.

In working out one scheme of calculation which is more acceptable, schemes (1) and (4) must be accepted, since sequence $R_{s,t,0} \to R_{s,15,0} \to S$ is already accepted by International Oceanographic Tables [3]. This one scheme may be envisioned in the form of

$$X_{s,t,p} \to [X_{s,t,p}/(X_{35,15,0} \cdot f(t) \cdot y(P)) = R_{s,t,p}] \to [R_{s,t,p} + \Delta_p = R_{s,t,0}] \to$$
$$[R_{s,t,0} + \Delta_{15} = R_{s,15,0}] \to S = f(R_{s,15,0}) \quad (5)$$

where $f(t) = X_{35,t,0}/X_{35,15,0}$ is the temperature dependence of specific electroconductivity of water with salinity 35 °/₀₀; $y(P) = X_{35,t,p}/X_{35,t,0}$ is the dependence of specific electroconductivity of normal water with salinity 35 °/₀₀ on pressure.

Appraisal of Allowable Error in Calculating Salinity

In examining the error in the calculation of salinity, it is necessary to consider the deviation of the calculated value from the real one in the case where there is no systematic error in the measurement of salinity by means of electroconductivity and where there is no experimental error in the measurement of specific electroconductivity, temperature and pressure. As all laws of interrelation of salinity with electroconductivity are arrived at through experiment, then the allowable error in calculating salinity on one hand, will be bounded by the errors in these researches. On the other hand, more stringent requirements for accuracy of definition for salinity enter into the calculation of density. For this case, the allowable error in calculating salinity will be defined at the present time by the reliability of the equation for the composition of seawater.

In reference [9] it is stated that the r.m.s. divergence, $\delta\sigma t$, between the measured and calculated density anomaly σ_t equals 0.011. Assuming that this divergence is determined independently by the errors of measurement of electroconductivity δ_X, temperature δ_t, pressure δ_p and calculation of salinity $\delta_{calc.}$, it can be written as:

$$\partial\delta_t = \sqrt{\left(\frac{\partial\sigma t}{\partial X}\,\delta_X\right)^2 + \left(\frac{\partial\sigma t}{\partial t}\,\delta_t\right)^2 + \left(\frac{\partial\sigma t}{\partial p}\,\delta_p\right)^2 + \left(\frac{\partial\sigma t}{\partial S}\,\delta_{calc}\right)^2} \qquad (6)$$

Taking

$$\frac{\partial\sigma t}{\partial X}\,\delta_X = \frac{\partial\sigma t}{\partial t}\,\delta_t = \frac{\partial\sigma t}{\partial p}\,\delta_p = \frac{\partial\sigma t}{\partial S}\,\delta_{calc}$$

we get the r.m.s. allowable error of calculation of salinity

$$\delta_{calc} \leq \frac{\delta\sigma t}{\left.\frac{\partial\sigma t}{\partial S}\right|_{max}\sqrt{4}} = \frac{0{,}011}{2} = 0{,}0055\ °/_{oo}$$ a.

where $\left.\frac{\partial\sigma t}{\partial S}\right|_{max} \approx 0{,}8\ \frac{1}{°/_{oo}}$. The maximum error equals $\Delta S_{calc} = 0{,}0165\ °/_{oo}$.

a. Appears arithmetically wrong - transl. note.

Knowing the error in calculating salinity, one may find the allowable error of constants and formulas of the separate expressions of the chain (5). This evaluation may be carried out, assuming that all errors have a random character and are not dependent on one another. Then the following relationship will be reliable:

$$\Delta S_{calc} = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \sigma_4^2 + \sigma_5^2 + \sigma_6^2} \tag{7}$$

where

$$\sigma_1 = \frac{\partial S}{\partial X_{35,15,0}} \Delta X_{35,15,0}, \quad \sigma_2 = \frac{\partial S}{\partial f(t)} \Delta f(t), \quad \sigma_3 = \frac{\partial S}{\partial y(P)} \Delta y(P)$$

$$\sigma_4 = \frac{\partial S \Delta(\Delta p)}{\partial \Delta}, \quad \sigma_5 = \frac{\partial S}{\partial \Delta_{15}} \Delta(\Delta_{15}), \quad \sigma_6 = \frac{\partial S}{\partial f(R_{S,15,0})} \Delta f(R_{S,15,0})$$

Allowing equality of subradical components, we obtain the maximum error Z_i of any constant or formula in chain (5)

$$\Delta z_i \leq \frac{\Delta S_{calc}}{\sqrt{6}} \frac{1}{\partial S/\partial z_i} = \pm 0{,}0067 \cdot \frac{1}{\partial S/\partial z_i} \tag{8}$$

Consequently, the maximum total error in calculating S_{calc} is assessed in the expression

$$\Delta S_{calc} = \sum_{i=1}^{6} \frac{\partial S}{\partial z_i} \Delta z_i \tag{9}$$

on the basis of real or expected errors of constants or formulas.

Units of Measurement

Separate constants and analytic expressions going into the scheme of calculating salinity (5), depend upon the chosen units of measurement. From the time of development of standard dilutions [14,16,17] to the present time there have come about some changes in units of measurement of specific electroconductivity, pressure, and the International Practical Temperature Scale has changed twice. Because of this, when measuring specific electroconductivity one must take into account the differences between International and absolute ohm, since 1,000 5 (Int'l ohm)$^{-1} \cdot$cm^{-1} = 1 (ohm absolute)$^{-1} \cdot$cm^{-1} = 0,01 mho$\cdot$M^{-1}.

The relationship connecting temperature measurements by IPTS-28 (t_{28}), IPTS-48 (t_{48}) and IPTS-68 (t_{68}), is expressed in the range 0-100°C by the equations [15]:

$$t_{28} = t_{48}$$

$$t_{68} = (1\text{-}4{,}88\cdot10^{-4})t_{48} + 5{,}8\cdot10^{-6}t_{48}^2 \qquad (10)$$

The new unit of pressure, the Pascal, is related to the bar:

$$1 \text{ Pascal} = 10^{-5} \text{ bar} = 10^{-4} \text{ dbar}$$

We will note that errors in calculating relative electroconductivity $R_{s,t,p}$ do not arise from the units of measurement only when the units of measurement of the values of specific electroconductivity $X_{s,t,o}$, pressure P and temperature scale completely coincide with units of electroconductivity $X_{35,15,0}$, made use of in finding dependency y(P) and f(t) respectively. In the case where the constancy of units of measurement is not observed, possible errors in calculating $R_{s,t,p}$ may reach .03 °/₀₀ in salinity equivalent.

Short Characteristics of Research on Relationship
Chlorinity - Salinity - Electroconductivity
of Seawater

Authors & Character of Research	Electrocond: specific X, (ohm Int'l)$^{-1}$ cm^{-1} Relative - R	Density ρ Salinity S °/₀₀ Chlorinity Cℓ °/₀₀	Temp. t, °C	Pressure	Remarks
Thomas, Thompson, Utterback, 1934. Measurement of specific electroconductivity of seawater in various regions & in various depths of Pacific & Indian Oceans and Mediterranean Sea at different values of chlorinity & temperature.	$X = (1,84-59,32)\cdot10^{-3}$ Reproducibility-0.01% $\Delta X=0.01-0.07 \times 10^{-3}$ Where S = 36,39 °/₀₀ t = 25°C	Cℓ=1,48-21,40 (S=2,7-38,7)	0,0; 5,0; 10,0; 15,0; 30,0 IPTS-28 Δt=±0,02	Atmospheric	Low salinity samples obtained by dilluting with distilled water.
Bein, 1935. Measurement of specific electroconductivity of seawater taken in the North Atlantic & Indian Oceans, the Kattegat Straits, Red, Mediterranean & Arabian Seas at different values of density and temperature.	$X = (9,00-62,0)\cdot10^{-3}$ $\Delta X=0,022\cdot10^{-3}$	P = 8-32 (S = 10,5-42)	0-25 IPTS-28 Δt=±0,01	Atmospheric	
Reeburgh, 1965. Measurement of specific electroconductivity from Red Sea & Normal water series P-37 (Cℓ19,369°/₀₀) and P-39 (Cℓ19,372°/₀₀) at different values of temperature and atmos. pressure.	$X=(23,45-70,79)\cdot10^{-3}$ $\Delta X = \pm0,001\cdot10^{-3}$	Cℓ=15,83-21,82 (S=28,60-39,42) ΔCℓ=±0,002 (ΔS=±0,0036)	-1-35 with interval of 2°C IPTS-48 Δt=±0,001	Atmospheric	Low chlorinity (salinity) samples obtained by dilluting with distilled water.

(cont'd)

(cont'd)

Authors & Character of Research	Electrocond: specific X, (ohm Int'l)$^{-1}$ cm^{-1} Relative - R	Density ρ Salinity S °/₀₀ Chlorinity Cℓ °/₀₀	Temp. t, °C	Pressure	Remarks
Bradshaw & Schleicher, 1965. Research on dependency of electroconductivity of seawater on hydrostatic pressure.	$X_{s,t,p}/X_{s,t,o} = Y(P,t,s)$; $\Delta Y(P,t,s)=\pm 7\cdot 10^{-5}$	S=31; 35; 39; $\Delta S = \pm 0,03$	0; 5,0; 10,0; 15,0; 20,0; 25,0; IPTS-48 $\Delta t=\pm 0,02$	Hydrostatic pressure 0-10338 dbar	
Cox, Culkin & Riley, 1962-1967. Research on the relationship of relative electroconductivity with chlorinity (salinity) of seawater, taken from different regions & different depths of all oceans, Mediterranean, Red, Black and Baltic Seas.	R = 0,09-1,16	Cℓ=1,38-23,00 (S=2,49-41,55) ΔCℓ=±0,001	14-29 IPTS-48	Atmospheric	Low salinity samples obtained from natural seawater of Black and Baltic Seas and dilluted water of high salinity with river waters.
Brown & Allentoft, 1966. 1. Research on inter-relationship between salinity & relative electroconductivity of seawater taken from various regions & depths of the Atlantic, Pacific & Indian Oceans; Mediterranean & Red Seas. 2. Research on the temperature dependency of normal waters at atmospheric pressure.	R = 0 + 1,6 $\Delta R = 2,2\cdot 10^{-6}$	S = 0-60	0; 5,0; 10,0; 15,0; 20,0; 25,0; 30,0; IPTS-48	Atmospheric	Low salinity samples obtained by dilluting with distilled water. High salinity samples obtained by evaporation. Salinity was measured by gravimetric dillution.

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